SHIMADZU
Excellence in Science

Application News

High Performance Liquid Chromatograph Mass Spectrometer LCMS-8060RX

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water in Accordance with EPA 533

Yui Higashi and Nami Iwasa

User Benefits

- The LC/MS/MS Method Package for PFAS in Drinking Water eliminates the need to configure analytical condition settings because it includes a ready-to-use method file in accordance with EPA Method 533.
- The LCMS-8060RX can accurately measure PFAS in spike-and-recovery tests at concentrations as low as one-fourth of EPA's Final MCLs.

■ Introduction

Per- and polyfluoroalkyl substances (PFAS) are widely used in various field and industries. But their structural stability and resistance to decomposition means they easily accumulate in the environment, and are suspected of being harmful to humans. Therefore, the U.S. Environmental Protection Agency (EPA) and the European Chemicals Agency (ECHA) have been implementing measures to strengthen PFAS-related regulations in recent years.

In April 2024, the EPA announced final maximum contaminant levels (final MCLs) 1). So it is important to use techniques capable of analyzing final MCLs of PFAS compounds with high sensitivity and accuracy.

This article describes the overall process, from sample preparation to measurement, and results from analyzing 25 target PFAS compounds (Table 1) in drinking water based on EPA method 533 2). Good results were obtained from using the LCMS-8060RX system with the LC/MS/MS Method Package for PFAS in Drinking Water for spike-and-recovery tests in ultrapure water and drinking water.

■ LCMS-8060RX

Samples were analyzed using a triple-quadrupole mass spectrometer, LCMS-8060RX (Fig. 1). The LCMS-TQ RX series offer the same high sensitivity and high speed performance as previous models with UF technology, but they also include the new CoreSpray technology, which can generate a more uniform nebulizer flow and provide more consistent measurements than previous models.

■ LC/MS/MS Method Package for PFAS in Drinking Water

Samples were analyzed using the LC/MS/MS Method Package for PFAS in Drinking Water, which is compliant with EPA methods 533 and 537.1. Because the package includes method files that are pre-optimized for LC/MS/MS analysis, that eliminates the time and effort involved in configuring analytical condition settings, so analysis can be started as soon as the instruments, reagent, and column are ready.

Fig. 1 LCMS-8060RX

Table 1 Analyte List

#	Compound	Sample Type
1	PFBA	Target
2	PFMPA	Target
3	PFPeA	Target
4	PFBS	Target
5	PFMBA	Target
6	PFEESA	Target
7	NFDHA	Target
8	4:2 FTS	Target
9	PFHxA	Target
10	PFPeS	Target
11	HFPO-DA	Target
12	PFHpA	Target
13	PFHxS	Target
14	ADONA	Target
15	6:2 FTS	Target
16	PFOA	Target
17	PFHpS	Target
18	PFNA	Target
19	PFOS	Target
20	9Cl-PF3ONS	Target
21	8:2 FTS	Target
22	PFDA	Target
23	PFUnA	Target
24	11Cl-PF3OUdS	Target
25	PFDoA	Target
26	13C4-PFBA	Isotope Dilution Analogues
27	13C5-PFPeA	Isotope Dilution Analogues
28	13C3-PFBS	Isotope Dilution Analogues
29	13C2-4:2FTS	Isotope Dilution Analogues
30	13C5-PFHxA	Isotope Dilution Analogues
31	13C3-HFPO-DA	Isotope Dilution Analogues
32	13C4-PFHpA	Isotope Dilution Analogues
33	13C3-PFHxS	Isotope Dilution Analogues
34	13C2-6:2FTS	Isotope Dilution Analogues
35	13C8-PFOA	Isotope Dilution Analogues
36	13C9-PFNA	Isotope Dilution Analogues
37	13C8-PFOS	Isotope Dilution Analogues
38	13C2-8:2FTS	Isotope Dilution Analogues
39	13C6-PFDA	Isotope Dilution Analogues
40	13C7-PFUnA	Isotope Dilution Analogues
41	13C2-PFDoA	Isotope Dilution Analogues
42	13C3-PFBA	Isotope Performance Standards
43	13C2-PFOA	Isotope Performance Standards
44	13C4-PFOS	Isotope Performance Standards

■ Sample Preparation

Samples were pretreated by adding 20 µL of the isotope dilution analogue in water, which was then extracted by solid phase extraction using an anion exchange solid phase column. The eluate from the solid phase column was concentrated by a factor of 250 by drying with nitrogen gas and then adding 80 % methanol to the volume. Then 10 µL of an isotope performance standard was added before analysis. A flow diagram of the pretreatment process is shown in Fig. 2.

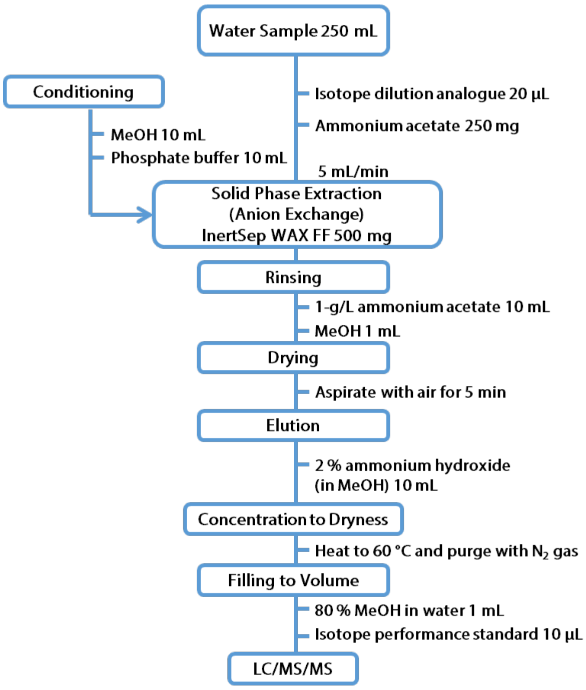

Fig. 2 Sample Preparation Process

■ Analytical Conditions

HPLC and MS analytical conditions are indicated in Table 2. The LC/MS/MS method package was used for analysis. Measuring PFAS requires particular care due to the risk of leaching PFAS from the system, mobile phase, or other sources. For this analysis, a delay column was installed between the mixer and autosampler to inhibit the effects of PFAS contamination from the system. A reagent intended for PFOS/PFOA analysis was used in the mobile phase.

Table 2 Analytical Conditions

UHPLC (Nexera™-X3 System)	
Analytical Column:	Shim-pack™ GIST HP C18 (50 mm × 2.1 mm I.D., 3 µm, P/N: 227-30039-02)
Solvent Delay Column:	Shim-pack GIST C18 (50 mm × 3.0 mm I.D., 5 µm, P/N 227-30015-03)
Mobile Phase A:	5 mM Ammonium Acetate in reagent water
Mobile Phase B:	Methanol
Gradient Program:	B 5 % – 40 % (1.0 min) – 95 % (8.0 – 10.0 min) – 5 % (10.1 – 15.0 min)
Flowrate:	0.25 mL/min
Column Temp.:	45 °C
Injection Volume:	2 µL
Run Time:	15 min

MS (LCMS-8060RX)	
Ionization:	ESI (Negative mode)
Mode:	MRM
Nebulizing Gas:	3 L/min
Drying Gas Flow:	5 L/min
Heating Gas Flow:	15 L/min
DL Temp.:	150 °C
Block Heater Temp.:	250 °C
Interface Temp.:	100 °C
MRM Transition:	Refer to LC/MS/MS Method Package for PFAS in Drinking Water

■ Measuring Standard Solutions

Nine standard solutions for calibration curve (0.2 to 100 ng/L in terms of water sample concentration and 0.05 to 25 µg/L in terms of solution concentration) were prepared, and each concentration was measured five times. Area for target compounds were calculated as the total of both straight and branched chains. The calibration curve coefficient of correlation (R) and concentration accuracy for each compound are indicated in Table 3.

Good results were achieved with calibration curve coefficient of correlation (R) greater than 0.997 and accuracy within the 85 to 130 % range for all concentrations. MRM chromatograms of 25 target components for 0.4 ng/L concentrations in water are shown in Fig. 3. Good peak shapes were obtained even at less than one-tenth of EPA final MCL.

Table 3 List of Calibration Curve Coefficient of Correlation (R) and Accuracy

#	Compound	Sample Type	R	Accuracy at Each Concentration (ng/L in Water)								
				0.2	0.4	1	2	4	10	20	40	100
1	PFBA	Target	0.9992	114.9	109.3	103.2	99.1	99.9	90.6	92.2	92.5	97.9
2	PFMPA	Target	0.9992	97.9	101.1	104.3	102.2	105.0	95.2	96.9	96.2	101.1
3	PFPeA	Target	0.9992	116.6	108.0	102.1	99.9	100.4	90.4	91.9	92.6	98.0
4	PFBS	Target	0.9993	98.6	102.0	99.5	103.3	104.5	96.4	96.0	96.2	102.6
5	PFMBA	Target	0.9990	94.6	99.1	106.4	103.6	105.9	95.1	97.2	97.2	101.6
6	PFEESA	Target	0.9978	105.4	109.8	106.0	102.9	104.2	92.2	92.1	90.9	95.8
7	NFDHA	Target	0.9989	129.2	115.6	100.8	96.7	97.6	86.8	87.5	87.9	92.4
8	4:2 FTS	Target	0.9985	99.5	110.8	98.8	99.5	104.3	93.2	98.1	95.5	98.8
9	PFHxA	Target	0.9992	110.3	106.1	103.4	99.8	101.8	91.5	93.2	94.3	99.4
10	PFPeS	Target	0.9984	103.4	104.2	106.1	103.4	106.0	94.6	92.6	94.3	96.0
11	HFPO-DA	Target	0.9991	94.3	100.4	104.4	102.5	106.6	94.7	97.3	98.3	102.6
12	PFHpA	Target	0.9988	107.3	109.2	103.8	99.4	101.0	91.0	94.1	94.0	99.7
13	PFHxS	Target	0.9995	97.1	101.2	98.8	101.7	102.9	96.8	96.1	99.3	103.9
14	ADONA	Target	0.9991	102.5	104.9	102.1	100.3	103.9	93.1	95.6	95.7	102.0
15	6:2 FTS	Target	0.9991	103.5	97.4	102.0	101.8	107.2	94.5	95.6	98.3	101.6
16	PFOA	Target	0.9994	129.9	110.1	100.8	96.6	98.6	89.2	89.5	89.8	95.4
17	PFHpS	Target	0.9989	97.1	100.5	103.8	99.6	108.2	96.5	96.8	98.5	97.7
18	PFNA	Target	0.9989	117.7	113.2	103.3	98.7	100.3	89.0	91.4	92.2	96.3
19	PFOS	Target	0.9992	129.6	113.8	100.4	96.3	97.4	87.0	87.7	89.7	93.0
20	9Cl-PF3ONS	Target	0.9972	95.0	105.7	106.9	105.1	106.4	94.1	94.3	94.4	97.6
21	8:2 FTS	Target	0.9988	101.1	95.6	94.9	101.5	105.0	95.3	100.0	96.6	105.6
22	PFDA	Target	0.9988	105.7	109.1	103.4	100.2	101.1	91.7	93.5	94.2	99.8
23	PFUnA	Target	0.9988	99.6	105.6	103.5	101.5	104.0	93.5	95.0	95.5	100.9
24	11Cl-PF3OUdS	Target	0.9976	99.0	102.6	106.4	101.3	106.7	95.3	94.6	95.4	98.7
25	PFDoA	Target	0.9993	105.1	105.7	103.3	100.0	102.7	93.0	95.3	95.3	100.6

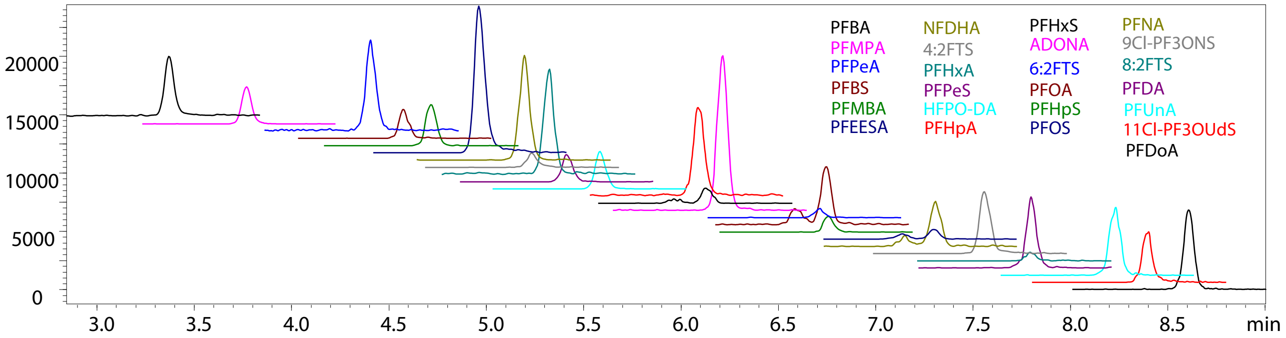

Fig. 3 MRM Chromatograms of 0.4 ng/L in Water (0.1 µg/L in Solution)

■ Spike and Recovery Tests in Ultrapure Water

Spike-and-recovery tests using ultrapure water were performed at concentrations less than EPA final MCLs. Ultrapure water was spiked with 1 and 4 ng/L in water of target compounds and pretreated according to the sample preparation process in Fig. 2. Good results were achieved with recovery rates within the 89 to 125 % range for all compounds, as shown in Fig. 4. Repeatability results were also good, with %RSD less than 20 % for all compounds, as shown in Fig. 5. The results confirmed good accuracy even for spike-and-recovery tests at low concentration levels.

As shown in Fig. 6, good results were obtained from evaluating isotope dilution analogues and isotope performance standards added in accordance with EPA method 533. All the recovery rates for isotope dilution analogues (#26 to 41) were within the 80 to 115 % range, and the recovery rates calculated based on average area during the development of the calibration curve for isotope performance standards (#42 to 44) were all within the 95 to 110 % range.

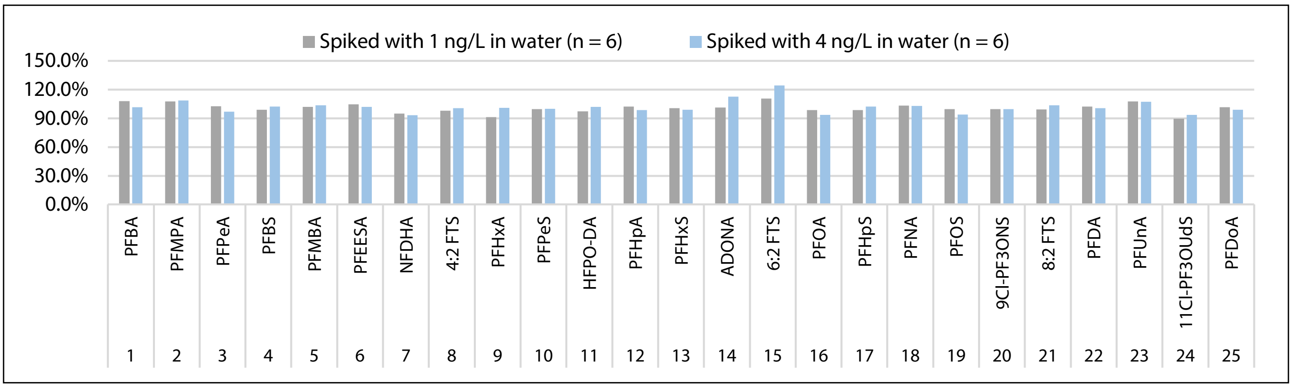

Fig. 4 Recovery Rate Results from Spike and Recovery Tests Using Ultrapure Water

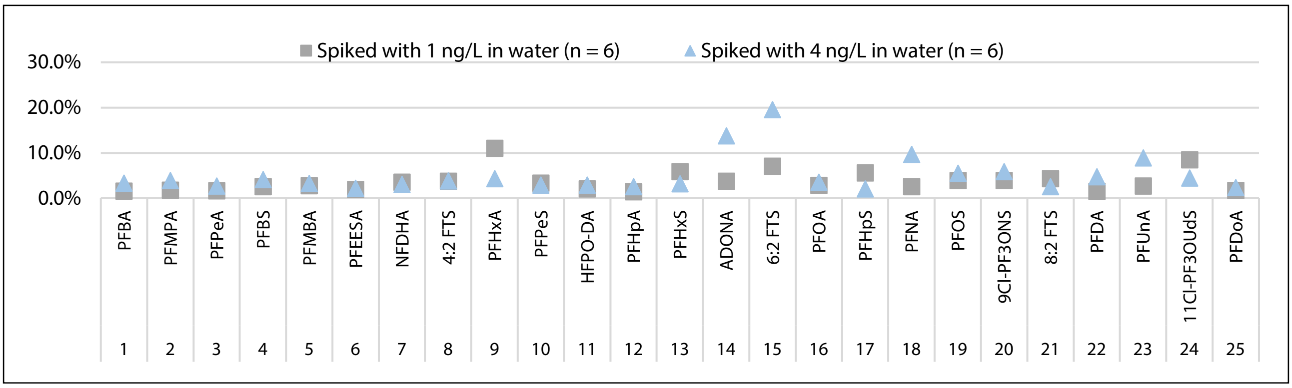

Fig. 5 Repeatability Results from Spike and Recovery Tests Using Ultrapure Water

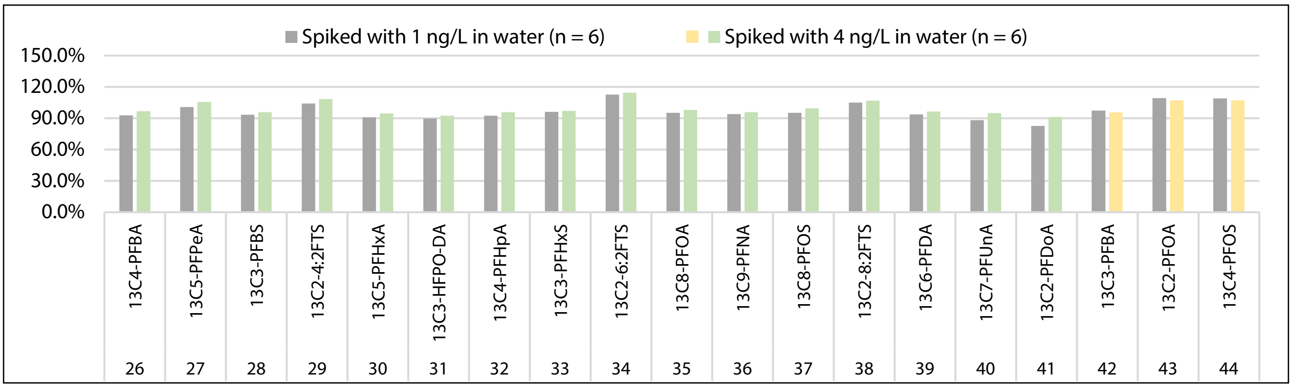

Fig. 6 Recovery Rates for Isotope Dilution Analogues (#26 to 41) and Isotope Performance Standards (#42 to 44) Using Ultrapure Water

■ Spike and Recovery Testing in Drinking Water

Spike-and-recovery tests using drinking water were performed at a concentration of 4 ng/L in water. The EPA method specifies preparing two spiked samples, a laboratory fortified sample matrix (LFSM) and a laboratory fortified sample matrix duplicate (LFSMD). Variability is evaluated based on a relative percent difference (RPD) value calculated from those two samples.

The LFSM and LFSMD recovery rate and %RPD are indicated in Fig. 7.

It shows good results with recovery rates within the 85 to 115 % range. With RPD less than 11 %, good results were even obtained from spike-and-recovery tests using drinking water. For the RPD calculation method, refer to EPA method 533.

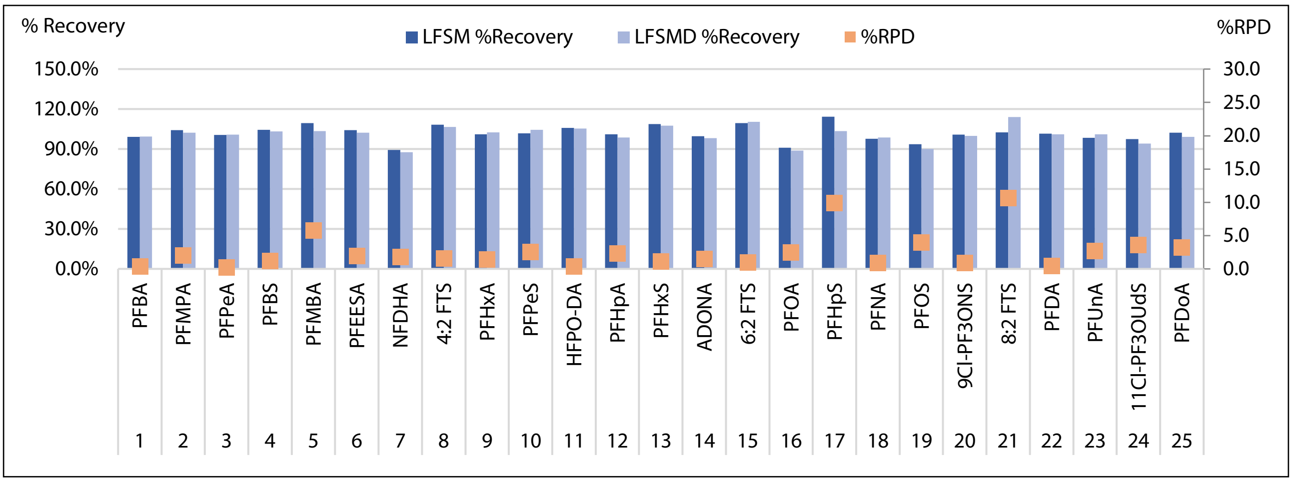

Fig. 7 Recovery Rates and RPD Results from LFSM and LFSMD (Spiked with 4 ng/L in water) Using Dinking Water

■ Conclusion

The LCMS-8060RX was able to analyze the 25 PFAS components specified as targets by EPA method 533 at concentrations less than one-tenth of the final maximum contaminant levels (final MCLs) published by the EPA (4 ng/L PFAS, 4 ng/L PFOS, 10 ng/L PFHxS, 10 ng/L PFNA, and 10 ng/L HFPO-DA). In spike-and-recovery tests using ultrapure and drinking water, the system provided good recovery rates and reproducibility results even when spiking at concentrations lower than the final MCLs specified by the EPA. The above results demonstrate that the LCMS-8060RX can be used to simultaneously analyze low concentrations of PFAS components in drinking water with good accuracy. In addition, the PFAS method package according to the EPA method 533 was used in the analysis. Because the package contains pre-optimized LC/MS/MS analysis method files, it reduced the labor required for determining analytical conditions.

Reference Documents

1) Per- and Polyfluoroalkyl Substances (PFAS)
Final PFAS National Primary Drinking Water Regulation
https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

2) Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry
Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry | US EPA

Shimadzu Corporation
www.shimadzu.com/an/

01-00785-EN First Edition: Dec. 2024

Related Products Some products may be updated to newer models.

LCMS-TQ RX Series Triple Quadrupole LC-MS/MS

Triple Quadrupole LC-MS/MS

LC/MS/MS Method Package for PFAS in Drinking …

Shim-pack GIST Series

HPLC Column Solutions

Related Solutions

Environment

Water

PFAS

Price Inquiry

Product Inquiry

Technical Service / Support Inquiry

Other Inquiry